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Dye-Sensitized Solar Cells for Space Power

Final Technical Report

for the

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Dye-Sensitized Solar Cells for Space Power

ABSTRACT

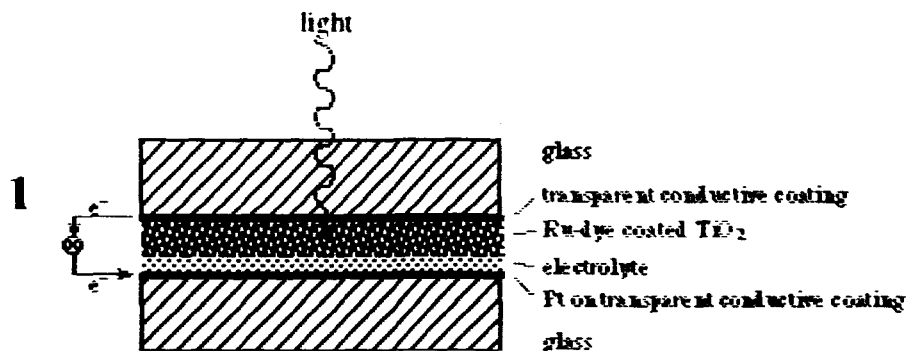
During the course of this grant, dye-sensitized solar cells were prepared and characterized. The solar cells were prepared using materials (dyes, electrolytes, transparent conductive oxide coated glass, nanocrystalline TiO_2) entirely prepared in-house, as well as prepared using materials available commercially. Complete cells were characterized under simulated AM0 illumination. The best cell prepared at NASA had an AM0 efficiency of 1.22% for a 1.1 cm^2 cell. Short circuit current (I_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) for the cell were 6.95 mA, 618 mV and 42.8%, respectively. For comparison purposes, two commercially prepared dye-sensitized solar cells were obtained from Solaronix SA, Aubonne, Switzerland. The Solaronix cells were also characterized under simulated AM0 illumination. The best cell from Solaronix had an active area of 3.71 cm^2 and measured an AM0 efficiency of 3.16%, with I_{sc} , V_{oc} and FF of 45.80 mA, 669.6 mV and 52.3%, respectively. Both cells from Solaronix were rapid thermal cycled between -80°C and 80°C . Thermal cycling led to a 4.6% loss of efficiency in one of the cells and led to nearly a complete failure in the second cell.

Introduction

Photovoltaic power is used on almost all space missions. It is the power source of choice for the International Space Station, military and commercial satellites, as well as future space probes to our neighboring planets. There are many benefits associated with using solar power for space applications. It allows the vehicle to be continually powered and self-contained after deployment, and there is no waste or byproduct that is generated and has to be removed or disposed of during operation. From an environmental standpoint, there is minimal impact on the environment from their use, and they produce far more energy than is consumed during their construction.

During the past decade, a new type of photovoltaic technology has emerged from the laboratory, which has the potential to reduce the cost/kW-hr of power generated by photovoltaic

devices by an order of magnitude over current technology.¹⁻⁴ The new solar cells are thin-film devices that use an organometallic Ru dye to harvest energy. The device (1) is composed of a glass substrate with a thin conductive coating of SnO_2 , a layer of nanocrystalline anatase TiO_2 sensitized with the Ru dye, an electrolyte layer, and a counter electrode which can be another layer of SnO_2 that has been coated with a thin layer of platinum. The cells have typically used a liquid electrolyte mixture containing I^- and I_3^- , and must be sealed to prevent leakage and degradation. However, dye-sensitized cells using solid electrolytes have recently been demonstrated.⁵ In the cell (Figure 1), a photon of light is absorbed by the Ru dye and promotes an electron into an excited state. The excited Ru complex then injects an electron into the conduction band of the TiO_2 particle to which it is bound, and the electron is conducted through the anatase layer to the back contact. To complete the circuit, the oxidized Ru complex is reduced by species in the electrolyte solution (I^- in this case). The reducing species in the electrolyte is in turn reduced at the counter electrode by an electron arriving from the external circuit. For this process, the incident photon-to-current conversion efficiency (quantum efficiency) has been reported to approach 100% for monochromatic light, and working cells have been measured with efficiencies over 10% at AM 1.5 solar radiation.²



These photovoltaic devices offer several advantages over current technology. Unlike current solar cells, the dye-sensitized cells do not require ultra-high purity materials, which will keep production costs down. TiO_2 is available inexpensively in bulk quantities, since it is used in many industrial applications as a white pigment. The ruthenium complex is expensive on a per gram basis, but a few milligrams of the complex can sensitize several square meters of solar cells.³ Additionally,

assembly of the cells is straight forward and amenable to mass production. A 10% efficient cell operating for 15 years is estimated to cost \$1/peakwatt.⁶ The costs can be further reduced with alternative flexible substrates and new black dyes.⁶ Specific power for these cells is projected to be 2000 watts per kilogram. These cells have also demonstrated good longevity by operation under continuous illumination at ambient temperatures for over 14,000 hours, corresponding to approximately 20 years of operation and 100 million turnovers of the dye.^{6,7}

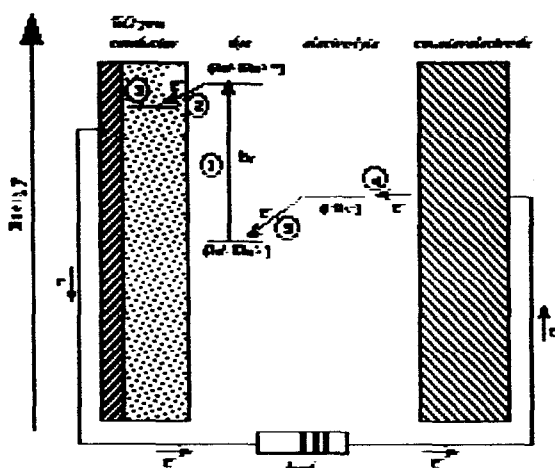


Figure 1. Schematic diagram of a dye sensitized photovoltaic cell, giving approximate energy levels of the electrons in each phase. The numbering scheme follows the flow of an electron through the circuit. Adapted from 4.

Project Results and Discussion

The organometallic ruthenium complex is the heart of the working cell, with the Ru atom continually cycling between Ru^{2+} and Ru^{3+} oxidation states. To date, the most successful dyes have 2,2'-bipyridine-4,4'-dicarboxylate ligands attached to the metal, but many other complexes have been evaluated.^{2,8-10} Ruthenium dyes are ideal because they have broad electronic absorption bands that closely resemble the solar spectrum between 400 and 750 nm. The carboxylate groups on the ligands act to tie the Ru molecules to the TiO_2 layers both structurally and electronically. Initially, we prepared our own ruthenium dyes in-house from RuCl_3 , 2,2'-bipyridine-4,4'-dicarboxylic acid and KSCN , but characterization results of the compounds were ambiguous. In an effort to standardize

our cell fabricating processes, dye was purchased from Solaronix SA, Aubonne, Switzerland. All of the data presented here was obtained using the Solaronix dye, $[\text{Ru}(\text{H}_2\text{dcpbpy})_2\text{NCS}_2]$ (where $\text{H}_2\text{dcpbpy} = 2,2'$ -dipyridyl-4,4'-dicarboxylate).

Titanium dioxide is readily available from many manufactures, however the particle size and distribution varies widely among manufacturers. We used TiO_2 from both Aldrich Chemical Company and from Degussa Corporation. Degussa's "P 25" had the smallest particle size and most uniform size distribution. However, to better standardize the cell assembly process, prepared TiO_2 pastes were also obtained from Solaronix SA. Cells were fabricated using in-house prepared TiO_2 as well as, TiO_2 from Solaronix. Cells prepared using the Solaronix paste consistently performed better than cells prepared with TiO_2 from other sources. We attribute the better performance to smaller particle size in the TiO_2 paste from Solaronix.

The conductive oxide coated glass also plays a major role in the quality of the device prepared. We investigated three types of conductive oxide coated glass: indium doped tin oxide (ITO), aluminum doped zinc oxide (Al:ZnO_2) and fluorine doped tin oxide (F:SnO_2). The ITO and F:SnO_2 coated glasses were obtained from commercial sources, and the Al:ZnO_2 was prepared in-house. The best results were obtained using the F:SnO_2 coated glass. The F:SnO_2 coating was more robust, was less susceptible to degradation from atmospheric humidity, and retained a higher conductivity than the other types of coatings.

Coating the back contact with a thin layer of platinum enhances the properties of the conductive oxide coated glass. The platinum not only increase the electrical conductivity, it also catalyzes the reduction of I_3^- to I^- , (which is an integral part of the internal electron transfer process in the cells) and improves the overall cell performance. The platinum was deposited onto the oxide coated glass by one of two methods: electrochemical deposition from a 1.22 mM H_2PtCl_6 aqueous solution and electron beam (e-beam) evaporation. Cells prepared using e-beam deposited platinum performed better than cells prepared with electrochemical deposited platinum films. The better performance is attributed to higher purity of the films produced by e-beam deposition.

Although the goal of the project is to eventually use solid electrolytes, for this phase only liquid electrolytes were used. Both a commercial electrolyte (Solaronix Iodolyte) and an electrolyte that was prepared at NASA (containing 0.3M LiI and 0.03M I₂ in acetonitrile) were evaluated. Cells filled with the in-house electrolyte produced remarkably higher current densities than cells using Iodolyte. However, Iodolyte is reported to have a much lower vapor pressure/higher boiling point than electrolytes using acetonitrile (boiling point = 170°C vs. 82°C for acetonitrile). Potential leaking/sealing of the electrolyte is a critical issue, especially for cells that would be used in space. To evaluate the leaking potential of cells contain the different electrolytes, cells containing either Iodolyte or the acetonitrile based electrolyte were sealed with Amosil 4 (a two part epoxy) and exposed to high vacuum ($<1 \times 10^{-7}$ torr) for over a month at room temperature. Nether cell type exhibited any signs of leakage or sealant failure.

All fabricated cells were characterized under simulated AMO illumination. The IV curve for the best cell fabricated at NASA GRC is presented in figure 2. The front half of the cell was prepared by depositing 4 μm of Solaronix Ti-Nanoxide T TiO₂ onto F:SnO₂ coated glass. The back half of the cell was F:SnO₂ coated glass that had been coated with platinum. The cell was filled with the acetonitrile-based electrolyte and sealed with Amosil 4. The 1.1 cm² active area cell had a measured efficiency of 1.22%. Short circuit current (I_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) for the cell were 6.95 mA, 618 mV and 42.8%, respectively.

For comparison purposes, two complete cells were obtained from Solaronix SA and upon receipt were characterized under AM0 illumination (Fig. 3, Table 1). The cells from Solaronix had active areas of approximately 3.7 cm² and were sealed with a thin film polymer hot melt (Surlyn 1702).¹¹ Following characterization, the cells were stored in a desiccator at room temperature for 52 days while waiting to be rapid thermal cycled and during this time received only limited exposure to ambient light. Prior to thermal cycling, the cells were again characterized under calibrated, simulated AM0 illumination (Fig. 4, table 1). It was observed that one of the cells (cell 1) had a substantial decrease in performance, and the second cell (cell 2) had only a modest loss of performance. The

large drop in current for cell 1 is simply attributed to it being a faulty cell. As mentioned in the introduction, these cells have demonstrated long lives.

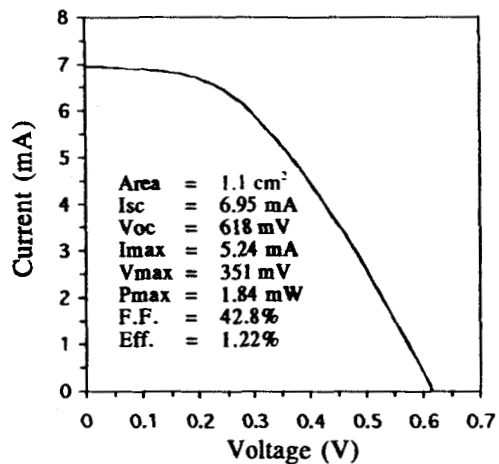


Figure 2. IV curve measured under simulated AM0 illumination for the best dye-sensitized cell prepared at NASA GRC.

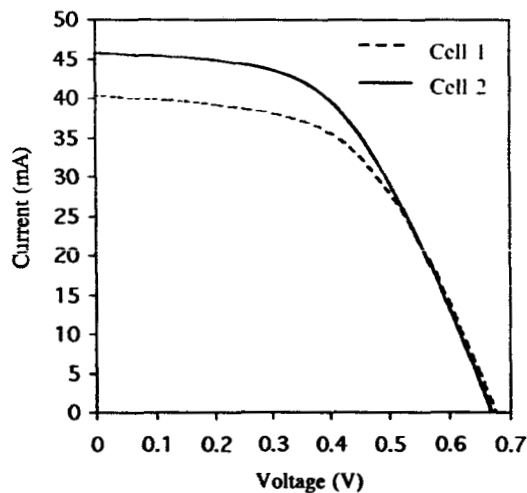


Figure 3. IV curves measured under simulated AM0 illumination for Solaronix cells when initially received.

Table 1. Air mass zero (AM0) characterization data for Solaronix dye-sensitized cells upon receipt, prior to rapid thermal cycling and following rapid thermal cycling.

	Initial AM0 Measure	Pre-cycling Measure	Post-cycling Measure
Cell 1, area	3.68 cm ²	3.68 cm ²	3.68 cm ²
Isc	40.3 mA	14.3 mA	10.8 mA
Voc	677 mV	687 mV	663 mV
I _{max}	32.4 mA	11.1 mA	8.76 mA
V _{max}	454 mV	499 mV	472 mV
P _{max}	14.7 mW	5.55 mW	4.13 mW
F.F.	53.9	56.3	57.6
Eff.	2.92 %	1.10 %	0.82 %
Cell 2, area	3.71 cm ²	3.71 cm ²	3.71 cm ²
Isc	45.8 mA	41.4 mA	36.5 mA
Voc	670 mV	672 mV	657 mV
I _{max}	37.7 mA	33.4 mA	30.0 mA
V _{max}	426 mV	404 mV	431 mV
P _{max}	16.0 mW	13.5 mW	12.9 mW
F.F.	52.3 %	48.5 %	54.0 %
Eff.	3.16 %	2.66 %	2.54 %

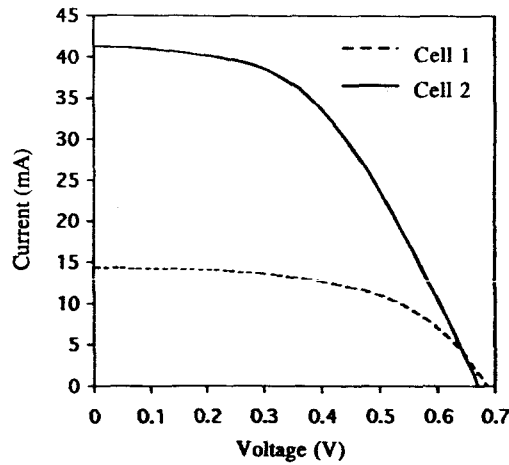


Figure 4. IV curves measured under simulated AM0 illumination for Solaronix cells following storage and prior to rapid thermal cycling.

Following the second AM0 characterization, the cells were rapid thermal cycled between -80°C and 80°C , which roughly corresponds to the temperature swings the cells would experience in a low-earth orbit. A spacecraft in low-earth orbit endures approximately 6000 thermal cycles per year. For our initial testing of the cells, they were rapid thermal cycled 100 times, which corresponds to six days in orbit. After thermal cycling, the cells were once again characterized under AM0

illumination (Fig. 5, Table 1). There was a measurable decrease in the performance of both cells, with that of cell 1 being the most dramatic. Upon examination, cell 1 lost a substantial amount of electrolyte during thermal cycling. The electrolyte appears to have escaped under or through the Surlyn seal, as the seal was stained yellow on one side of the cell following thermal cycling. Physically, cell 2 survived the thermal cycling reasonably well, with no signs of electrolyte loss. However, it did have a 4.6% drop in efficiency, caused mainly from a decrease in current produced by the cell.

In general, current dye-sensitized solar cells lack long-term stability at elevated temperatures ($>60^{\circ}\text{C}$).⁷ However, due to our limited amount of data, it is difficult to determine whether the decrease in performance of cell 2 was from the elevated cycle temperatures, or some other failure mechanism. A more extensive study is in progress. As mentioned above, the lack of stability of cell 1 is likely due to a defective cell. This is evident from the thermal cycling data and the loss of electrolyte during cycling. Although Surlyn 1702 has a reported softening temperature of 65°C , if the failure of cell 1 had been caused from excessive heating of the cells, both cells would have been expected to exhibit the same loss of electrolyte during rapid thermal cycling.

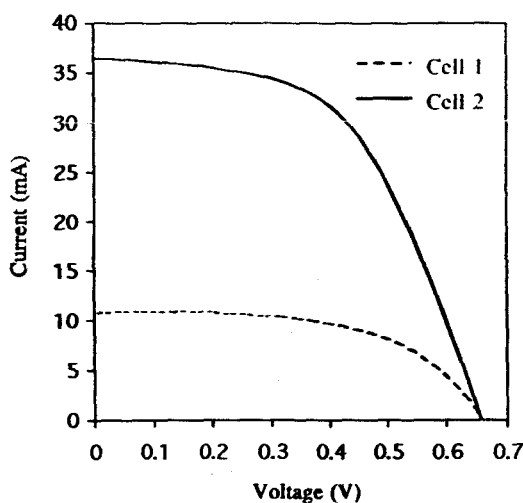


Figure 5. IV curves measured under simulated AM0 illumination for the Solaronix cells following rapid thermal cycling (100 cycles from -80°C to 80°C).

Concluding Remarks

The focus of this phase of the project was to do an initial screening of the cell components and to optimize our assembly technique. So far we have determined the best configuration of TiO_2 /conductive oxide coated glass/electrolyte that give the highest efficiency. In addition, the first space environmental characterization of nanocrystalline dye-sensitized solar cells has been initiated. So far the cells have survived the testing fairly well. One of the chief complaints about these types of cells is the liquid electrolyte and the long-term sealing concerns of these cells in the vacuum of space. The liquid electrolyte containing cells were exposed to pressures less than 1×10^{-7} torr and exhibited no signs of sealant failure. The loss of performance associated with rapid thermal cycling needs to be further investigated. Additionally, it was determined that the performance of this type of cell is dependent on the length of time they were "light soaked" prior to cell characterization. The longer they were light soaked, the better their measured performance. The optimal light soaking time needs to be further investigated.

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